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Pressure Induced Static Magnetic Order in Superconducting FeSe_{1-x}

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We report on a detailed investigation of the electronic phase diagram of FeSe_{1-x} under pressures up to 1.4 GPa by means of AC magnetization and muon-spin rotation. At a pressure $\simeq 0.8$ GPa the non-magnetic and superconducting FeSe_{1-x} enters a region where long range static magnetic order is realized above T_c and bulk superconductivity coexists and competes on short length scales with the magnetic order below T_c . For even higher pressures an enhancement of both the magnetic and the superconducting transition temperatures as well as of the corresponding order parameters is observed. These exceptional properties make FeSe_{1-x} to be one of the most interesting superconducting systems investigated extensively at present.

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The phase diagram of the recently discovered Fe-based high-temperature superconductors (HTS) [1] share a common feature with cuprates and heavy fermions. The parent compounds of the Fe-based HTS, such as, LnOFeAs ($\text{Ln}=\text{La, Ce, Pr, Sm}$) [2, 3, 4, 5, 6, 7, 8, 9], AFe_2As_2 ($\text{A} = \text{Ba, Sr, Ca}$) [10, 11, 12, 13] and $\text{Fe}(\text{SeTe})$ [14, 15] exhibit long-range static magnetic order. Upon doping or application of pressure (chemical or external), magnetism is suppressed and superconductivity emerges. Recent investigations revealed, however, that the structurally most simple binary compound FeSe_{1-x} is an exception of this rule [16]. Different from the other Fe-based HTS, FeSe_{1-x} did not seem to exhibit static magnetic order for pressures up to about 30 GPa [16]. Yet, short-range spin fluctuations, which are strongly enhanced towards T_c , were observed [17]. The superconducting transition temperature of FeSe_{1-x} was found to increase continuously to $\simeq 37$ K at 7 – 9 GPa. For higher pressures a decrease is observed with $T_c \simeq 6$ K approaching 20 GPa [16, 18]. Subsequent experiments with finer pressure steps revealed, however, a local minimum on $T_c(p)$ at 1.5 GPa of unexplained nature [19].

In this letter we report on a detailed study of the evolution of the superconducting and magnetic properties of FeSe_{1-x} as a function of pressure and temperature through a combination of AC susceptibility and muon-spin rotation (μSR) techniques. Two samples with the nominal composition $\text{FeSe}_{0.94}$ and $\text{FeSe}_{0.98}$ were investigated. The obtained phase diagram of FeSe_{1-x} was found to be separated into three distinct regions. At low pressures, $0 \leq p \lesssim 0.8$ GPa, the samples are nonmagnetic and T_c increases monotonically with increasing pressure. In the intermediate pressure region, $0.8 \leq p \lesssim 1.0$ GPa, $T_c(p)$ decreases with increasing pressure and static magnetism develops. In this region of the phase diagram the superconducting and the magnetic order parameters co-

exist and compete on a short length scale. Incommensurate magnetic order, which sets in above T_c , becomes partially (or even fully) suppressed below $T_c(p)$. At higher pressures, $p \gtrsim 1.0$ GPa, $T_c(p)$ shows a tendency to rise again. The magnetic order becomes commensurate and both, bulk magnetism and bulk superconductivity coexist within the whole sample volume.

FeSe_{1-x} samples with the nominal composition $\text{FeSe}_{0.94}$ and $\text{FeSe}_{0.98}$ were prepared by solid state reaction similar to that described in Refs. 20, 21, 22. Powders of minimum purity 99.99% were mixed in appropriate ratios, pressed and sealed in a double-walled quartz ampoule. The pressed rod was heated up to 700°C followed by annealing at 400°C [22].

The pressure was generated in a piston-cylinder type of cell especially designed to perform muon-spin rotation experiments under pressure [23]. As a pressure transmitting medium 7373 Daphne oil was used. The pressure was measured in situ by monitoring the pressure shift of the superconducting transition temperature of Pb or/and In. Two types of cells, the first one made from CuBe alloy [maximum pressures $p_{max}(300\text{ K}) \simeq 1.4$ GPa and $p_{max}(7\text{ K}) \simeq 1.1$ GPa] and the second one made from MP35 alloy [$p_{max}(300\text{ K}) \simeq 1.7$ GPa and $p_{max}(7\text{ K}) \simeq 1.4$ GPa], were used.

AC susceptibility measurements were performed by using a home made AC magnetometer with a measuring field $\mu_0 H_{AC} \sim 0.1$ mT and frequency $\nu = 96$ Hz. In order to keep the position of the sample unchanged during the series of AC susceptibility under pressure measurements, the excitation and the two pick-up coils were wound directly on the cell. To ensure that the AC signal was entirely determined by the Meissner response of individual grains and not by the Josephson type of weak links between them, measurements of the AC susceptibility as a function of ν ($0 \leq \nu \leq 599$ Hz) and

H_{AC} ($0 \leq \mu_0 H_{AC} \leq 0.5$ mT) at $T = 2.5$ K on a standard Quantum Design PPMS instrument were performed. The experiments reveal that the AC magnetization (M_{AC}) scales linearly with H_{AC} and is independent on ν as expected for a superconductor in the Meissner state.

The zero-field muon-spin rotation (ZF μ SR) experiments were carried out at the μ E1 beam line at the Paul Scherrer Institute, Switzerland for the temperatures ranging from 0.25 to 50 K. The typical counting statistics were $\sim 7 \cdot 10^6$ positron events for each particular data point.

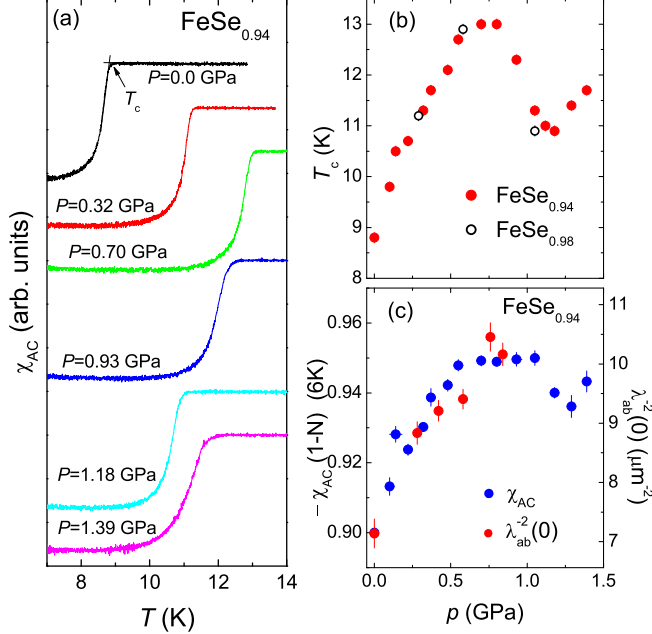


FIG. 1: (a) Temperature dependence of χ_{AC} of FeSe_{0.94} measured at (from the top to the bottom) $p = 0.0, 0.32, 0.7, 0.93, 1.18$, and 1.39 GPa. The transition temperature T_c is determined from the intersection of straight line fits to the data above and below the transition. (b) Dependence of T_c on p of FeSe_{0.94} and FeSe_{0.98}. (c) Pressure dependence of the normalized AC susceptibility $-\chi_{AC}(1-N)$ at $T = 6$ K and the inverse squared in-plane magnetic penetration depth λ_{ab}^{-2} at $T = 0$ K [25].

The response of the superconducting state of FeSe_{1-x} to pressure was studied in AC susceptibility (χ_{AC}) experiments, Figure 1. The transition temperature T_c , Figure 1b, shows a non-monotonic increase with a local minimum at $p \simeq 1.2$ GPa, similar to $T_c(p)$ reported by Miyoshi *et al.* [19]. Figure 1c depicts $-\chi_{AC}(T)(1-N)$ at $T = 6$ K. Here N denotes the demagnetization factor which, assuming a spherical shape of the sample grains, was taken to be equal to $1/3$. For temperatures lower than T_c , $|\chi_{AC}(T)(1-N)|$ is smaller than unity due to the penetration of the AC magnetic field on a distance λ from the surface of each individual grain (λ is the magnetic penetration depth). Following Shoenberg [24], χ_{AC}

in a granular sample is expected to scale with λ^{-2} , which is the case here, as may be seen from the comparison of $\chi_{AC}(6$ K) with $\lambda_{ab}^{-2}(T = 0)$ obtained in transverse field μ SR experiment [25].

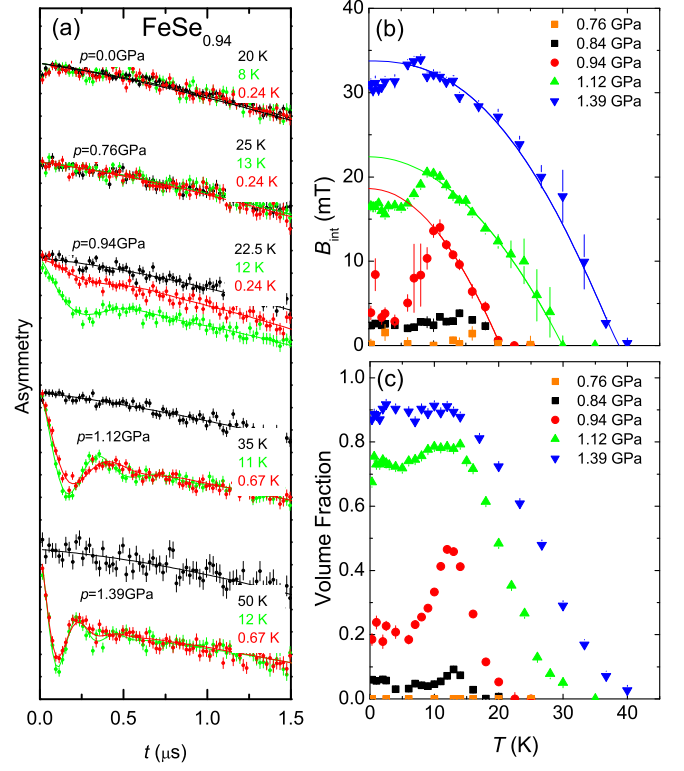


FIG. 2: (a) Zero-field μ SR time-spectra of FeSe_{0.94} measured at (from the top to the bottom) $p = 0.0, 0.76, 0.94, 1.12$, and 1.39 GPa. Dependence of the internal field at the muon stopping site B_{int} which is proportional to the magnetic order parameter (b), and the magnetic volume fraction (c), on temperature at various pressures. The solid lines in panel **b** are the fit of $B_{int}(T)$ in the region $T_c(p) \leq T \leq T_N$ to $B_{int}(T) = B_{int}(0)[1 - (T/T_N)^\alpha]^\beta$ (α and β are the power exponents).

The magnetic response of FeSe_{1-x} was studied in ZF μ SR experiments. In the following we discuss the ZF μ SR data for the three different pressure regions.

In the low-pressure region, $0 \leq p \lesssim 0.8$ GPa, where T_c increases with increasing p , the ZF μ SR time-spectra prove the absence of long range magnetic order for all temperatures as exemplified by the identical weakly damped spectra for $T = 0.24$ K, near $T_c(p)$ and 20 K, see $p = 0.0$ and $p = 0.76$ GPa data in Figure 2a. The solid lines in Figure 2a correspond to a two-component fit:

$$A^{ZF}(t) = A_S^{ZF}(t) + A_{PS}^{ZF}(t). \quad (1)$$

with the first component describing the sample response and the second one representing the contribution of the pressure cell (ZF responses of the CuBe and MP35 cells are described in [23]). The sample contribution is well

fitted to the single-exponential decay function [26]:

$$A_S^{ZF}(t) = A_{S,0}^{ZF} e^{-\Lambda_0 t}, \quad (2)$$

(Λ_0 is the exponential relaxation rate), thus revealing that very diluted and randomly oriented magnetic moments exist in the sample volume which can be attributed to small traces of Fe impurities, see Ref. 26.

In the intermediate pressure region, $0.8 \leq p \lesssim 1.0$ GPa, the spontaneous muon-spin precession is clearly observed in the ZF μ SR time spectra, see $p = 0.94$ GPa data in Figure 2a. Therefore, long range magnetic order is established below the Néel temperature T_N . The analysis of the μ SR data was made by accounting for the separation of the sample into magnetically ordered regions with muons experiencing a static local field and nonmagnetic (paramagnetic) regions:

$$A_S^{ZF}(t) = A_{S,0}^{ZF} \left[m \left(\frac{2}{3} j_0(\gamma_\mu B_{int} t) e^{-\Lambda_T t} + \frac{1}{3} e^{-\Lambda_L t} \right) + (1-m) e^{-\Lambda_0 t} \right]. \quad (3)$$

Here m is the magnetic volume fraction of the sample, j_0 is a zeroth order Bessel function, $\gamma = 2\pi \cdot 135.5$ MHz/T is the muon gyromagnetic ratio, and Λ_T and Λ_L are the exponential relaxation rates longitudinal and transverse to the initial muon-spin polarization. The oscillating part of the signal was found to be good described by a Bessel function, which is archetypical for incommensurate magnetic order [27]. The dependence of the internal field B_{int} , corresponding to the magnetic order parameter, and the magnetic volume fraction on temperature are shown in Figures 2b and c.

For pressures above 1.0 GPa we observe a further increase of the magnetic volume fraction and of the internal magnetic field B_{int} , Figure 2. Additionally, we find that the μ SR lineshape is better described by a damped cosine with zero initial phase rather than by a Bessel function:

$$A_S^{ZF}(t) = A_{S,0}^{ZF} \left[m \left(\frac{2}{3} \cos(\gamma_\mu B_{int} t) e^{-\Lambda_T t} + \frac{1}{3} e^{-\Lambda_L t} \right) + (1-m) e^{-\Lambda_0 t} \right]. \quad (4)$$

This suggests that in the high pressure region the magnetic order becomes commensurate.

Figure 3 summarizes our results on the magnetism and superconductivity in an electronic phase diagram for FeSe_{1-x} . The magnetic order coexists and competes with superconductivity for $p \gtrsim 0.8$ GPa. Above this pressure long range magnetic order is established below $T_N > T_c$ and bulk superconductivity sets in below T_c . The competition of the two ground states in this pressure range is evident from the following two observations: First, as a function of pressure T_c is weakened as soon as magnetic order appears, leading to the local maximum at

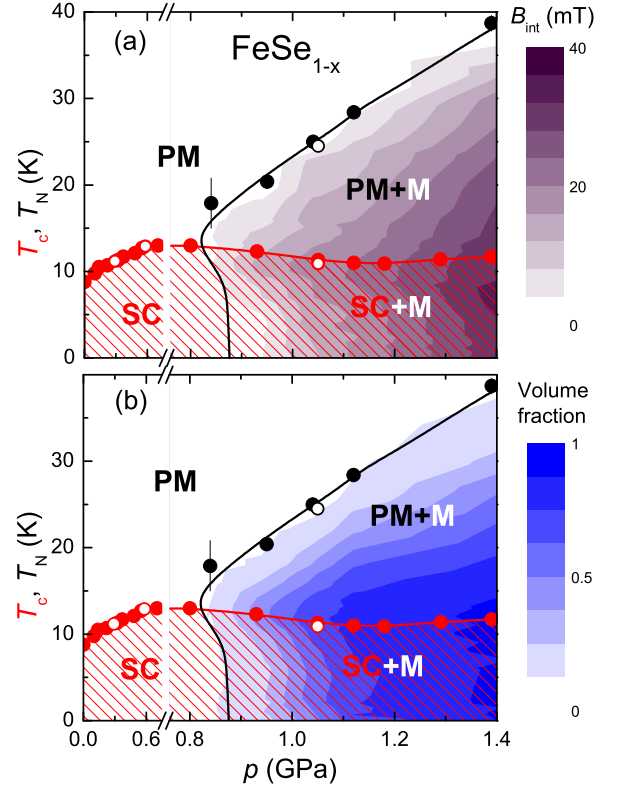


FIG. 3: (a) Pressure dependence of the superconducting transition temperature T_c , the magnetic ordering temperature T_N , and the internal field B_{int} (magnetic order parameter) obtained in AC susceptibility and muon-spin rotation experiments. (b) Pressure dependence of T_N , T_c , and the magnetic volume fraction. The $T_c(p)$ and $T_N(p)$ lines are guides for the eye. The closed and the open symbols refer to $\text{FeSe}_{0.94}$ and $\text{FeSe}_{0.98}$ sample. SC, M, and PM denote the superconducting, magnetic and nonmagnetic (paramagnetic) states of the sample.

$p \simeq 0.8$ GPa in $T_c(p)$. Second, as a function of temperature B_{int} , as well as the magnetic volume fraction, decrease below T_c showing that the magnetism, which develops at higher temperatures, becomes partially (or even fully) suppressed by the onset of superconductivity. The superconducting volume fraction is close to 100% for all pressures, Figure 1c, while the magnetic fraction increases continuously and reaches $\simeq 90\%$ at the highest pressure investigated $p \simeq 1.39$ GPa, Figure 2c. In other words, both ground states coexist in the full sample volume at $p = 1.39$ GPa. Our data do not provide any indication for macroscopic phase separation into superconducting and magnetic clusters (bigger than a few nm in size), as observed e.g. for $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [28]. Actually, the data rather point to a coexistence of both order parameters on an *atomic* scale. This scenario is compatible with the itinerant two-band models of Fe-based HTS proposed recently by Vorontsov *et al.* [29] and Cvetkovic and Tesanovic [30]. According to these models the transition between the magnetic and the su-

perconducting states may involve the formation of the intermediate phase, where both superconductivity and magnetism coexist.

In conclusion, the magnetic and superconducting properties of FeSe_{1-x} were studied as a function of pressure up to 1.4 GPa by means of AC magnetization and muon-spin rotation techniques. Above $\simeq 0.8$ GPa superconductivity was found to coexist with magnetism with Néel temperatures $T_N > T_c$. In a narrow pressure range, where a local minimum in $T_c(p)$ is observed, superconductivity competes with magnetism in the sense that the magnetic volume fraction and the magnetic order parameter are suppressed below T_c . At the highest pressure investigated here superconductivity and static long range commensurate magnetism coexist on short length scales in the full sample volume. Furthermore, both forms of order seem to be stabilized by pressure, since T_c as well as T_N and the magnetic order parameter simultaneously increase with increasing pressure. This exceptional observation provides a new challenge for theories describing the mechanism of high temperature superconductivity.

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